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(54) Title: PROCESS FOR RECOVERING INORGANIC COAGULANTS FROM WATER OR WASTE WATER TREATMENT SLUDGES

(57) Abstract

The invention is concerned with the recovery of inorganic coagulants used in water or waste water treatment processes from the coagulant-containing sludges produced in such processes. The method consists of the following steps: 1) treatment of the sludge with acidic or alkaline material as appropriate in order to dissolve the coagulant; 2) adjustment of liquor pH to 2 - 3, if necessary; 3) addition of polyelectrolyte and optionally a solid adsorbent to the liquor to cause precipitation of some impurities; 4) separation of the liquor containing dissolved coagulant from the residue; 5) contact of the supernatant from step 4 with a positively charged and/or hydrophobic solid adsorbent to remove soluble organic materials. The process described has the dual benefit of reducing the volume of sludge for disposal, and reducing the amount of fresh coagulant needed and hence saving on coagulant costs.

Process for recovering inorganic coagulants from water or waste water treatment sludges.

This invention is concerned with the recovery for recycling of inorganic coagulants used in water or waste water treatment processes from the coagulant–containing sludges produced in such processes. The process described has the dual benefit of reducing the volume of sludge for disposal, and reducing the amount of fresh coagulant needed and hence saving on coagulant costs.

Bibliographic details of the publications referred to in this specification are collected at the end of the description.

In order to satisfy the ever increasing thirst of our industrialised and urbanised societies, water authorities must turn to treatment of more and more polluted water sources using complex technologies. This creates a secondary problem – the disposal of residues/sludges formed as a result of the treatment. Usually such residues contain substantial quantities of inorganic coagulant such as aluminium or ferric hydroxides which create much bulk and make the sludge less than beneficial to the environment into which it is discharged.

Coagulants are used to encourage the agglomeration of colloidal impurities in many water/wastewater purification processes; commonly the agglomerated impurities are then removed from the product water by sedimentation or filtration. The coagulants may be either organic or inorganic in nature. The inorganic coagulants are usually based on iron or aluminium, most commonly used are aluminium sulphate (alum) or ferric sulphate or chloride.

Past attempts to recover and reuse alum in conventional water treatment processes were usually motivated by problems associated with the handling and disposal of the aluminium hydroxide containing sludges. Recovery of alum reduces the amount of solids and improves the dewatering and filtration characteristics of the residue. Reuse of the recovered alum also reduces the chemical cost.

alkali there are a number of problems to overcome. Firstly, the amount of acid or alkali required is affected by both the amount of water present and the age of the sludge. Because the cheap dewatering processes are slow the sludge ages during the process. Secondly, during redissolution, organic acids and heavy metals are liberated if present in the residue. Aged sludge requires lower pH for redissolution of the polymerised aluminium hydroxide which also increases the concentration of other undesirable components in the recovered stream. In the present state of the art only approximately 50–70% of the recovered coagulant can be reused safely.

To improve the aluminium recovery rate and to enhance its separation from impurities, techniques such as liquid ion exchange [(11)], electrochemical coagulant regeneration [(12)], ultrafiltration [(13)], and selective two-step aluminium recovery employing composite membrane [(14)], have been evaluated in the laboratory. It remains to be seen whether such techniques are economic in a practical situation.

Thus there is a need for a simple technique which would allow recovery of the inorganic coagulant selectively, leaving the unwanted impurities, such as humic and fulvic acids, behind. We have discovered a relatively simple separation process that meets this need and which may be incorporated into water treatment plants that use inorganic coagulants.

Accordingly this invention provides a method for recovering inorganic coagulants from water/wastewater treatment sludges in a condition which enables effective reuse of the coagulant, which method comprises the following steps:

1. Treatment of the sludge with acidic or alkaline material as appropriate in order to dissolve the coagulant.
2. Precipitation of humic acids by adjustment of liquor pH (usually to 2 – 3 .
3. Addition of polyelectrolyte and optionally a solid adsorbent to the liquor to cause precipitation of impurities.
4. Separation of the liquor containing dissolved coagulant from the residue.
5. Contact of the supernatant from step 4 with a positively charged and/or hydrophobic solid adsorbent to remove soluble organic materials.

Accordingly, in another aspect, this invention provides a process for recovery of inorganic coagulant from water treatment sludges which comprises steps 1 – 5 above, followed by (as and when necessary) subjecting the impurity coated positively-charged PC/H Adsorbent to a physical process thereby to remove the coating of impurities from the PC/H Adsorbent, separating the removed impurities from the PC/H Adsorbent and returning the cleaned PC/H Adsorbent to the process.

The process of the invention is further described in the following non-limiting examples.

EXAMPLE 1

A water treatment sludge was treated at pH 2.5 using dilute sulphuric acid. The liquor was then separated from the sludge and treated with polyelectrolyte to precipitate a second sludge. The supernatant from polyelectrolyte treatment was an aluminium rich solution with an initial colour of 460 PCU and a Total Organic Carbon (TOC) content of 190 mg/L. This solution was passed through columns of Amberlite IRA 910 in either the hydroxyl or sulphate form. The hydroxyl column eluent had an average colour of 100 PCU and TOC 40mg/L; the sulphate column eluent had an average colour of 120 PCU and 50mg/L TOC.

Each column passed all of the aluminium initially present.

When the impurity coated resins were washed with water, the hydroxyl column released impurities equivalent to 55% of the initial colour and 42% of the TOC while the sulphate column released 28% of the colour and 24% of the TOC. Further treatment of each column with 0.5M NaOH released impurities equivalent to 45% of the initial colour and 58% of the initial TOC from the hydroxyl column and 72% of the initial colour and 58% of the initial TOC from the sulphate column.

EXAMPLE 2

A sludge from the SIROFLOC® process was treated with acid at pH 2.5, a cationic polyelectrolyte was added to the supernatant from the acid treatment. A flocculant precipitate formed which was allowed to settle. The supernatant from the polyelectrolyte treatment had pH 2.95, an aluminium content of 317 mg/L, apparent colour = 1080 PCU, and TOC = 164 mg/L.

Table 5. Adsorption of humic substances from acidic regeneration effluent by ion exchange resins.

Type	Source	Code		Flow Rate BV/hr	Length of Run BV	Average Removal		Recovered by Regen.%		Efficiency Recovered Al %
						TOC	Col	TOC	Col	
Untreated regeneration effluent										72**
Monofunctional C_{18} sorbent	Millipore	C_{18} SepPak		12	70		49	ND	ND	ND
Trifunctional bonded C_{18} sorbent	Millipore	t C_{18} SepPak		20	80	76	82	ND	72	95
Styrene polymeric adsorbent	Rohm & Haas	1.1 ml bed XAD 2	Increas -ing	20	70	50	49	ND	48	88
"	"	XAD 4	Porosity	20	70	54	53	ND	38	ND
"	"	XAD 7	↓	20	70	58	59	ND	36	ND
Acrylic polymeric adsorbent	"	XAD 8	↓	20	70	54	52	ND	40	ND
Acrylic gel Type I	"	5 ml IRA 958		8.6	145	57	68	96	101	92
Styrene macroreticular Type II	"	5 ml IRA 910		8.6	115	54	59	98	88	92
Styrene DVB Macroreticular	"	5 ml IRA 904		8.6	100	60	59	117	104	ND
Activated carbon	Hydradarco			6	30	85	92	84	45	82
Silica gel				20	70	44	39	ND	56	ND
Cotton Wool				20	70	ND	39	ND	40	ND
Cellulose				6	70	ND	56	ND	16	ND

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CLAIMS

1. A method for recovering inorganic coagulants from water/wastewater treatment sludges in a condition which enables effective reuse of the coagulant, which method is characterised by the following steps:

   (1) treating the sludge with an acidic or alkaline material, as appropriate, in order to dissolve the coagulant to produce a liquor containing the dissolved coagulant from the sludge;

   (2) precipitating humic acids by adjustment of the pH of the liquor;

   (3) adding a polyelectrolyte, and optionally a solid adsorbent, to the liquor to cause precipitation of impurities;

   (4) separating the liquor containing dissolved coagulant from the residue;

and

   (5) contacting the supernatant liquor from step (4) with a positively-charged and/or hydrophobic solid adsorbent to remove soluble organic materials.

2. A method as claimed in Claim 1, characterised in that the impurity coated positively-charged and/or hydrophobic solid adsorbent ("PC/H adsorbent") obtained in step (5) is subjected to a physical process to remove the coating of impurities from the PC/H adsorbent, the removed impurities are separated from the PC/H adsorbent and the cleaned PC/H adsorbent is returned to process step (5).

3. A method as claimed in Claim 1 or Claim 2, characterised in that the polyelectrolyte is an anionic polyelectrolyte.

4. A method as claimed in any one of the preceding Claims, characterised in that the the adsorbent for step (3) is a natural or artificial clay mineral or a particulate carbon.

5. A method as claimed in any one of the preceding Claims, characterised in that the positively charged and/or hydrophobic adsorbent (the "PC/H Adsorbent") used in step (5)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 93/00281

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.[5] C02F 011/00; C02F 011/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC CO2F 011/00; C02F 011/12; C02B 001/20; C02C 003/00; C02C 005/02.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU:IPC as above

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT:IPC as above
search terms: coag: (for C02F 11/00 & 11/12); coag: and humic(s) acid and polyelectrolyte (for C02C 3/00 & 5/02; humic(s) acid and polyelectrolyte (for C02B 1/20). Chemical Abstracts: sludge and (water or H_2O or aque:) and coag: and (humic(s) acid).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A, 3959133 (METCALF & EDDY, INC.) 25 May 1976 (25.05.76)	1-6
A	US,A, 3901804 (KANZAKI PAPER MANUFACTURING CO. LTD.) 26 August 1975 (26.08.75).	1-6
A	Derwent Abstract Accession No. 13587Y/08, Class D15 F09, JP,A, 52-003256 (MITSUBISHI HEAVY IND KK) 11 January 1977 (11.01.77)	1-6

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU 93/00281

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	3901804	FR	2208846	JP	49065052	SE	388412

END OF ANNEX